

AN APPROACH TO THE USE OF
RADIOISOTOPES IN SALT SPRAY TESTING

by

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OBJECT

To study the feasibility of making the standard salt spray test more quantitative through the use of radiotracer techniques.

SUMMARY

Salt spray testing is a general qualitative technique used to evaluate metal surface protective coatings. The conclusions drawn from such testing are at present arbitrary since comparisons are made with standards which are sometimes not well defined and which depend upon individual judgment for determining conformity with specifications.

Since salt spray testing simulates the effects of several types of corrosion, it was felt that a wedging of the techniques used in measuring such corrosion with radioisotopic techniques might prove fruitful in making the salt spray test more quantitative. This report deals with the uses of radioisotopes to study corrosion mechanisms, corrosion rates, surface phenomena, etc., and can provide a point of departure for launching an investigation into quantitative salt spray testing.

INTRODUCTION

Laboratory Report 59-TM1-222 demonstrated the usefulness of isotopic methods in checking government specifications.¹ It showed that interpretations based on visual evidence alone, unsupported by quantitative information, can lead to erroneous conclusions. Thus, a visual specification test designed to provide a means of selecting grease barrier materials did not indicate the ability of the test grease to penetrate the material but indicated instead the penetrating ability of a dye used with the grease. The soundness of judgments of barrier materials based on test results obtained by this method need not be discussed further.

The determination by salt spray testing of the durability of surface coatings (organic or metallic) and of whether or not multiple-component devices will continue to function after such testing appears to be another case where the interpretation of the information obtained is usually considered less important than the manner in which the test is conducted. To determine how items will withstand corrosive atmosphere, specimens are carefully placed in special brine atmospheres where considerable attention is given to salt concentration, specimen location, angle of suspension, temperature, etc. After the test has been run for a specified time, or when failure of the coating or multiple-component occurs before the specified time, the test is stopped and the visible results are recorded. When the specified time is related to the go or no-go mechanical operation of a multiple-component device, no criticism can be made of this type of salt spray testing. But, in instances involving an evaluation of the behavior of surface coatings, the current practice of awaiting visible evidence of coating failure due to corrosive action can stand close scrutiny in relation to a more particular meaning of "failure." It is with this distinction in mind that this report is written, since it is intended to show that a means is available for making salt spray testing more quantitative and more sensitive.

DISCUSSION

The interaction of elemental metal with most environments generally explains why few metals are found in a pure state. Because of the extensive use of metals in modern technology, it is important to consider how this

¹C. White and R. Graybush, "The Use of a C14-Labeled Test Reagent To Determine Grease Proofness of Barrier Materials," Picatinny Arsenal, 1959.

reactivity and the environment combine to affect the usefulness of the metal. Where it is known that the effect of the environment is adverse, protective measures are taken by using special surface coatings (metallic or organic) which are known to be inert to the environment. If the coating is not inert then it must be capable of reacting with the environment to produce an inert barrier. The corrosive salt spray test is the standard means of measuring the durability of the coating by observing the elapsed time before failure. However, this general laboratory test is of only limited value in making qualitative judgments since the experimental conditions may not be duplicated by the field conditions. The conclusions drawn from the test are based on gross evidence, but they have been widely accepted because of a lack of impetus for applying more sensitive methods to obtain more precise information.

Standard salt spray testing procedure calls for the immersion of coated (organic or metallic) specimens in an atmosphere of salt spray vapor where salt concentration, temperature, and humidity are specified. The specimen is allowed to remain in the vapor atmosphere until there is visible evidence either that the surface has failed or that the surface is still intact on completion of some preselected time period. This procedure may take many hours to complete and the time required for the test may exceed the time in which microscopic surface failure occurs. This holds true for evaluating both surface failure and surface intactness. However, the appearance of the base metal is the only criterion that is used at present to determine whether the surface has or has not reacted with the corrosive environment.

It can be expected that any technique which would make possible the detection of base material in advance of visual indications of surface reaction would represent an advance in salt spray testing technique. Completion of the test would take less time and the data would give a truer indication of the actual condition of the surface coating.

Motivated by a desire to place the interpretation of salt spray testing on a sounder foundation, the Nucleonics Research Section of FRL, originally under the auspices of QAD, undertook an investigation of the use of isotope techniques to achieve greater sensitivity in salt spray testing. The use of such techniques would, without altering the general conduct of the salt spray test, make possible the achievement of the detection sensitivities characteristic of isotopic techniques (Table 1). The specific technique might be implemented either through neutron activation or by the use of radioisotopes available from standard commercial sources. Thus, the use

of nuclear detection equipment to show the presence of radioactive metal could provide more quantitative data on the fate of the protective plating and the base material.

TABLE 1
Detection sensitivities of several isotopes

Element	Half-life	Upper Limit of Sensitivity (μg)
Cr^{51}	27.8 d	5×10^{-3}
Fe^{56}	47 d	1×10^{-2}
Co^{60}	5.3 y	4×10^{-3}
Ni^{63}	2.6 h	9×10^{-4}
Cu^{65}	12.5 h	6×10^{-4}
Zn^{65}	52 m	1×10^{-2}
Cd^{113}	43 d	2×10^{-3}
Sn^{113}	27.5 h	7×10^{-4}

Techniques involving neutron activation would require that metal specimens be placed in a reactor where the interaction of thermal neutrons and the nuclei of metallic species would produce radioactive isotopes. The radioactivity of the isotopes produced would be an integral part of the specimen and could be used to indicate the presence of metals in very small concentrations. The use of commercially available isotopes as a substitute for neutron activation is possible, though incorporating them into any given material involves more handling. Depending upon the objective involved, it is conceivable that both sources of radioactivity might be used in a single experiment. The correlation of radioactivity with amount of metal might make possible the use of nuclear detection equipment to indicate the presence of radioactive metal and provide quantitative information concerning the fate of the protective plating as well as the base material. Koch lists detection limits obtainable for elements that are commonly used as protective plates.¹ The values listed in the last column

¹Koch, *Activation Analysis Handbook*, Academic Press, 1960.

represent the weight of element which will yield 1000 dpm after irradiation in a flux of 10^{14} n/cm/sec after saturation, or after a 30-day period if the half-life is more than 30 days long. It should be realized that large samples (50-100 g) could not be irradiated to the extent indicated by Koch's Table I since the radiation produced would present great handling problems. However, activity data for the small amounts of materials that can be measured by this technique indicates that, even after only partial activation by neutrons, it may be possible to detect corrosion products in smaller concentrations than have been measured up to the present.

The successful conclusion of an investigation yielding a definite technique could make possible more cogent interpretation of quantitative data and better prediction of surface coating behavior in order to provide for extended protection of metallic surfaces.

A literature search, conducted as a necessary preliminary to a planned investigation of salt spray corrosion, revealed that isotopes have not been used extensively in corrosion research. A review of the literature from 1946 to the present produced only 18 references dealing with radioisotopic studies of corrosion, and none of these references deal with salt spray corrosion. Because the reaction rates are slow and the amounts of materials involved are small, corrosion phenomena can readily be studied by radioisotopic techniques. The use of such techniques to study salt spray corrosion seems to be indicated by the results of studies of corrosion in general. Such studies indicate that principles derived from the investigations of other phases of the corrosion problem may be applicable to salt spray testing.

Most of the isotopic tracer studies of corrosion have been concerned with mechanisms (Refs 2, 4, 5, 7, 9, 10, 12, 14, 15, and 17). Such studies characterize the types of corrosion occurring in a system, explain how material is removed from metallic surfaces as a result of specific reactions, and relate the external influences connected with the reactions to a corrosion process. Principles derived from such studies may be used as a basis for conjecture as to why corrosion occurs in salt spray testing. Thus, principles are cited to account for the lack of reproducibility of laboratory tests and field tests as well as to explain why the surface should be active towards the brine, etc.¹

¹F. L. Laque, *Interpretations of Tests and Correlation With Service*, ASTM 32nd National Metals Congress and Exposition, Chicago, 1960.

Very little work is reported dealing specifically with corrosion rates (Refs 1, 2, 3). Usually such studies are concerned with solubilities of metals in electrolytes and the rates at which such solubilities cause metals to be removed from the surface. This type of study can be applied to incipient salt spray corrosion to determine what is happening to the surface before any change is visible. References 1, 2, and 3 deal specifically with solubility tests, and there is no reason why the approaches indicated in these studies cannot be applied to salt spray corrosion. The exposure of base metal has a microscopic beginning resulting from surface solubility, and isotopic techniques could supply the sensitivity necessary for determining the minute quantities of materials dissolved from the surface as well as escaping through the pores and pinholes resulting from corrosive action. A base metal made radioactive by neutron irradiation or plated with a layer of "hot" base metal could be used to check for microscopic corrosion by monitoring the salt spray wash for activity. Combining a radioactive protective coating and a radioactive base metal would make it possible to concurrently determine corrosion rates and the appearance of pinholes resulting from salt spray testing. Moreover, the detection of base metal would indicate the presence of pinholes in surfaces that, upon visual examination, had been declared intact, and would give some insight into discrepancies between laboratory test results and field test results. It can be reasoned that a test could proceed to a point where microscopic surface damage existed but was undetected because of the gross nature of the standard test.

The influence of radiation on corrosion (Refs 6, 12) arises wherever high activities are encountered. Although it might be anticipated that the activities needed to enhance detection efficiency in an incipient corrosion investigation could exhibit such effects, this phenomenon is not expected to be significant. Admittedly, the activity produced by neutron irradiation and required in such a study may be higher than is normally encountered in most laboratory work, but it would be below the levels which contribute to any deviations from normal behavior. Should doubt arise about the existence of radiation effects in a corrosion study, verification can be made by working with samples originating from radioactive material and by activating samples obtained from working with stable materials after the completion of experiments. By comparing the results obtained from the radioactive and non-radioactive materials, the influence of radiation can be determined.

Corrosion is, in general, a selective process occurring within localized areas of the surface. It can be ascribed to concentration effects and cathodic or anodic conditions produced by electrolyte and dissimilar metals.

Localized phenomena can account for surface solubility resulting in the breaching of a protective surface. This phase of corrosion can be considered as being concerned with the adsorption of ions and the active surface for such ions on plated surfaces. The areas involved in such adsorption are considered to be sites for specific reactions which result in surface solubility (Refs 8, 10, 11, 13, and 16). The amounts of adsorbed materials are small, assuming monolayer adsorption, and could be studied by using radioisotopic techniques. This approach could be expanded to include a study of salt spray corrosion as a function of surface treatment to determine how this factor is related to the failure of surface coatings.

All of the phases of corrosion mentioned above can be related directly to salt spray corrosion. In order to make corrosion testing more quantitative, it is intended to employ the tracer techniques previously established to study solubility rates and surface effects. The successful use of radioisotopes for similar studies indicates that this objective can be successfully pursued. The fact that special equipment may be needed in addition to the conventional equipment need not adversely affect the thought of undertaking such testing. The added cost of such equipment would be outweighed by the advantages to be gained from making the test more precise. Such equipment, though specialized, need not be too expensive.

The literature search was originally undertaken to determine to what extent radioisotopes had been employed in salt spray corrosion study. The sources searched disclosed no references specifically on the subject and there are relatively few references on corrosion and radioisotopic techniques generally.

However, it is felt that this general review will give the reader some idea of the scope of the field and serve also as a source of basic information on experimental techniques. This review has suggested to the authors that it may be possible to use the techniques in a general field to study phenomena in a particular field. It is hoped thereby that it may provide information for converting a purely qualitative test to a quantitative test which will be of greater value.

SOURCES

The following sources of information were examined:

Chemical Abstracts, 1946 to present

Review of Metal Literature, 1950 to present

Metal Finishing

Nucleus Science Abstracts, 1958 to present

Metallurgical Abstracts, 1958 to present

Journal of Electrochemical Society, 1957 to present

Chemical Engineering News, 1955 to present

Corrosion, 1958 to present

A.S.T.M. Standards, 1954 to present

Proceedings U.N. International Conference on Peaceful Uses of Atomic Energy, 1958

REFERENCES

1. Koch, R. C., *Activation Analysis Handbook*, Academic Press, 1960
2. Levin, A. I., and Falicheva, V. I., *Nauch. Doklady Vysshei Shkoly, Khim i Khim. Tekhnol.*, 1958, No. 1, pp 32-35; *Chemical Abstracts*, Vol 53, 1959, p 910e

This reference discusses the use of radioactive indicators in the study of corrosion by a superimposed current from the outside. The radioactive material used was Zn⁶⁵ with a half-life of 250 days in 0.5N H₂SO₄. In this medium, zinc has at first a specific activity equal to 6.5 mc/ml. The electrolytic corrosion of zinc was at its highest in the absence of current; then it decreased notably with an increase in the cathode polarization, and after attaining a definite value of "protective" potential, it stopped completely. The mechanism of the protective action of the current is apparently of an electrochemical nature, with the creation of a kind of barrier retaining Zn⁺⁺ in the double electric layer, thereby causing the process of self-solution of the metal to cease.

3. Anson, D., *Journal of Institute of Fuel*, Vol 32, pp 10-14 (1959); *Chemical Abstracts*, Vol 53, p 4081C, 1959

The use of a radioactive, hollow cylindrical steel probe makes it possible to establish the metal loss by a count of the radioactivity of the probe washings. It should be possible to obtain accurate results by using exposure times as short as 10 minutes and counting times of 2 minutes with conventional counting equipment.

4. Aziz, P. M., "Radioactive Tracers in the Study of Pitting Corrosion of Aluminum," *J. Electrochem. Soc.*, Vol 101P, p 120 (1954)

Radioactive cobalt and lead ions in solution have been used to study the distribution of local cathodes on aluminum alloy specimens which were actively pitting, and to study the process of film breakdown and repair on aluminum alloy specimens after introducing them into a corrosive environment. Radioactive ions were introduced into the solution in the pitting study, after the sample had been allowed to proceed for a predetermined length of time. The tracer was then plated out onto local cathodes, where after washing and drying of the cathodes, autoradiographs of the surface were prepared.

5. Brasher, D. M., and Stove, E. R., "Use of Radioactive Tracers in the Study of the Mechanism and Action of Corrosive Inhibitors," *Chemistry and Industry*, Vol 126, p 171 (1952)

This paper reports that radioactive chromium and the benzoate radicals remain on mild steel after washing. The influence of time of immersion of the steel in the solution of radioactive K_2CrO_4 and also of the concentration of the solution on the amount of chromium on the steel was studied.

6. Byalobzheskii, A. B., *Atmospheric Corrosion of Metals Under Radiation*,'' AEC-TR-3410 , Vol 13, No. 1, Jan 15, 1959, p 424

During irradiation under atmospheric conditions corrosion takes place underneath the moist film appearing on the surface of the metal as the results of condensation or adsorption of water vapor. Consequently this corrosion has an electrochemical nature as does the usual atmospheric corrosion.

7. Erwell, Lars G., "Radioactive Tracers in Corrosion Research," *Jernkontorets Annaler*, Vol 143, pp 646-72 (1959)

Stearic acid C¹⁴ in solutions as well as Radon or Xenon¹³¹ in a gas phase were used to study surface properties. Electroplating of a thin layer of Fe⁵⁵ on an iron surface permits studies of the initial stage of corrosion.

8. Byalobzheskii, A. V., "Influence of Ionizing Radiation on the Corrosion of Metals Under Atmospheric Conditions," *Zh. Fiz. Khim. XXXIII*, No. 6, June 1959, pp 1256-62

Experiments were conducted to study the effects of continuous exposure to salt spray on metals that had been irradiated. It appears that radiation appreciably increases the rate of salt spray corrosion.

9. Simnad, Massoud, T., *Proceedings U. N. Intern. Conference on Peaceful Uses of Atomic Energy*, Vol 19, pp 193-200 (1958)

The mechanism of the inhibition of corrosion by passivating agents such as chromates and phosphates has been studied with radioisotopes of chromium, phosphorus, and sulfur. The complicated process of adsorption, chemical interaction, and film formation may be followed readily by means of the tracer techniques. Radiochemical analysis and carrier techniques may be very effective in determining minute amounts of corrosion products from stainless steel.

10. Lewis, J. F., and Plumb, R. C., "A Radiochemical Technique for Determining the Specific Area of Aluminum Metal Surfaces," *International Journal of Applied Radiation and Isotopes*, Vol 1, pp 33-45 (1956)

It has been found that a phosphate and chromate acid mixture, which dissolves the oxide on an aluminum surface, deposits a thin film on the aluminum by reacting with it, but not by the reaction with oxide. The specific area of the aluminum surface may be determined by using radiochemical techniques, by comparing the amount of the film formed per unit of geometric area on a given sample with the amount of film formed per unit of area on a "flat" sample.

11. Herr, W., "Radiotracer Technique for Surface Measurement," *Angew. Chem.* 59A, p 155 (1947)

An attempt was made to determine the absolute surface area of metals by metal-ion adsorption using radio-lead, radio-bismuth, and radio-polonium, the assumption being that the ions were adsorbed as a monolayer. Unfortunately, it was found that the pickup was sensitive to other factors, such as other ions present in solution, and autoradiograms revealed that the activity picked up was not distributed uniformly.

12. Simnad, Massoud T., "Nuclear Irradiation and Radioisotopes in Metal Research," *International Journal of Applied Radiation and Isotopes*, Vol 1, pp 145-171 (1956)

This review covers a wide range of topics in the field of metal research where nuclear irradiation and radicisotopes have been employed. Nuclear irradiation has been used both as a means of detecting minute quantities of impurities and as a powerful tool for carrying out studies of the structure of metals. Radioisotopes have found applications in almost all branches of metal research, namely in studies of segregation, friction, vapor deposition, vapor pressure, slag metal reactions, electrolytic action on metal surfaces, and oxidation.

13. Iron-Steel Engineer, *Use of Radioactive Tracers in the Study of Corrosion*, Vol 31, 1954 (7), pp 130-133

A piece of metal was immersed in a corroding solution that contained radioactive material. A geiger counter was used to check activity on the metal surface, due to the exposure of the medium.

14. Simnad, Massoud T., and Ruder, R. T., "The Mechanism of Exchange Between Radioactive Ions in Solution and Metal Surfaces," *Transactions of Electrochemical Society*, Vol 98, p 301 (1951)

The metals were washed after various times of immersion in the solutions, their acquired radioactivities were measured, and the distributions of radioactive cobalt on the surfaces (shown by means of autoradiographs) were determined in order to ascertain how these parameters offset the exchange mechanism.

15. Schwabe, K., *Isotopentechnik*, May 1961, pp 175-178

The simplest feature of this review is that molecules or ions could be marked radioactively that could be adsorbed on a metal surface. The metal surface can then be immersed in a medium with marked molecules, whereby the remaining activity on the surface is measured by means of a counting tube or a scintillating counter.

16. Coriou, H., "Problems of Aqueous Corrosion in the Field of Nuclear Energy," *Bull. Inform. Sci. et Tech. (Paris)*, No. 49, pp 46-68, 1961; *Chemical Abstracts*, Vol 55, No. 18, p 17448, 1961

A brief review of different types of corrosion of metals and alloys is given, including corrosion at the grain boundaries, pitting, blistering corner attack, stress corrosion, and cavitation.

17. Willard, John E., "Applications of Radiotracers to the Study of Surfaces," *Journal of Physical Chemistry*, Vol 57, p 129, 1953

In this paper techniques and methods of tagged ion collection on metal receivers are discussed. Such studies will yield information on surface forces and the kinetics of reactions involving surface atoms, and will help to solve problems in the fields of metal plating, mirror formation, and corrosion prevention.

18. Oelsner, G., *Galvanotechnik*, Vol 51, pp 294-300 (1960); *Chemical Abstracts*, Vol 56, p 260 (1962)

This paper mentions the possibility of corrosion being due to oxygen reduction or the evolution of hydrogen. Several examples were cited, such as the change in corrosion potential of iron-zinc being different from that of iron-nickel. Values were listed for 56 metals under different pH and buffer conditions.